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Intense-Field Ionization of Monoaromatic Hydrocarbons using Radiation Pulses of Ultrashort Duration: Monohalobenzenes and Azabenzenes

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Synopsis Using 50-fs, 800-nm pulses, we study the intense-field ionization and fragmentation of the monohalobenzenes C_6H_5-X ($X=F, Cl, Br, I$) and of the heterocyclics azabenzene C_5H_5N (pyridine) and the three diazabenzenes $C_4H_4N_2$ (pyridazine, pyrimidine, and pyrazine). Avoiding focal intensity averaging we find indications of resonance-enhanced MPI. In the monohalobenzenes the propensity for fragmentation increases for increasing Z : fluorobenzene yields predominantly $C_6H_5F^{n+}$, while iodobenzene yields atomic ions with charges up to I^{8+} . We ascribe this to the heavy-atom effect: the large charge of the heavy halogens' nuclei induces ultrafast intersystem crossing to dissociative triplet states.

We report on the ultrafast intense-field photoionization and fragmentation of the four monohalobenzenes C_6H_5-X ($X=F, Cl, Br, I$) and of the heterocyclics azabenzene C_5H_5N (pyridine) and the three diazabenzenes $C_4H_4N_2$ (pyridazine, pyrimidine, and pyrazine). We investigate such systematic sequences of molecules to highlight the effect of changing a single parameter (e.g. the nature of the X atom) on the intense-field photodynamics. Data is recorded under intense-field, single-molecule conditions. We focus 50-fs, 800-nm pulses into the molecular vapor, and record ion mass spectra for intensities of 10^{13} to 10^{15} W/cm². Our ion mass spectrometer has an interaction volume of micrometer size in all three dimensions, which allows us to record ion yields without focal intensity averaging, i.e., for sharply determined intensities.

For the monohalobenzenes[1], the intensity-dependence of the ion yields indicates resonance-enhanced multiphoton ionization (REMPI). The intermediate 3-photon resonant state is the spin-singlet $^1(\pi, \pi^*)$ state in the phenyl ring. Remarkably, parent ionization strongly dominates for fluorobenzene and chlorobenzene, while for the heavier bromobenzene and, most notably, iodobenzene the formation of atomic halogen ions becomes dominant, with high charges (up to I^{8+}). Thus, for increasing Z of the halogen substituent, the dissociation rate increases dramatically. In iodobenzene, the iodine atom breaks away on a femtosecond timescale, i.e., so early in the pulse that it can ionize to the observed high charge states. We explain these observations though the so-called heavy-atom effect. A larger nuclear charge Z of the halogen substituent increases the spin-orbit coupling term in the molecular Hamiltonian, thereby fa-

cilitating an intersystem crossing (ISC) to the rapidly dissociating triplet state $^3(n, \sigma^*)$. In iodobenzene the ISC rate becomes fast enough to compete with optical pumping of the excited (neutral) state into the ionization continuum, and the branching ratio starts to favor dissociation over parent-ion formation.

The (di)azines[2] represent another systematic series of perturbations of the benzene molecule. Here, the perturbation is inside the phenyl ring: one or two C atoms in this ring are replaced by N atoms, creating heterocyclic molecules. Research on this target group allows us to study the effect of the nitrogen atoms' lone pairs (the in-plane N-atom sp^3 orbitals that point away from the ring). The three diazines have the same chemical formula, with the only difference being the relative placement of the two perturbing N atoms and their lone pairs (ortho-, meta-, para-substitution). For all targets, stable singly- and doubly-charged parent ions are observed, again with features indicating REMPI. Fragmentation dynamics differ greatly between molecules, with each species also showing evidence of metastable decay processes.[3]

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References

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